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# Comparison between Silicon Nanopillars Prepared by Bosch Process and Metal Assisted Chemical Etching

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# Comparison between Silicon Nanopillars Prepared by Bosch Process and Metal Assisted Chemical Etching

## Abstract

Nanopillars fabricated by Metal Assisted Chemical Etching (MacEtch) wet-etch process have been compared with those by Bosch dry-etch process. The Bosch process in this study gave vertical nanopillars with smooth side walls, which was better than the typical Bosch process. However, the verticality of the nanopillars depended on the location within the wafer where they were etched. On the other hand, MacEtch process gave a very consistent feature from 100 to 1000 nm diameter using 20 nm thick Au film without an expensive etching tool. The present technical report discuss the difference between MacEtch and Bosch processes.

## Keywords

Metal Assisted Chemical Etching, Bosch Process, Nanopillar


## Disciplines

Engineering | Life Sciences | Physical Sciences and Mathematics

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	Comparison between Silicon Nanopillars Prepared by Bosch Process and Metal Assisted Chemical Etching	Author: Rimjhim Chaudhary

### 1. Introduction

Silicon nanopillars have gathered an immense interest in nanofabrication industry due to their large surface area, which potentially can be explored in various fields as sensing, photovoltaics, microelectronics, optoelectronics, and photonics.<sup>1</sup> Vertical nanopillar arrays have an advantage of higher surface to volume ratio, resulting in higher sensitivity and signal to noise ratio. The goal of this project is to perform the on-site inspection of silicon nanopillars fabricated by Metal Assisted Chemical Etching (MacEtch) at Quattrone Nanofabrication Facility (QNF), and to compare them with nanopillars fabricated by Deep Reactive Ion Etching (DRIE) using Bosch process, which is a well-established deep silicon dry-etching technique.<sup>2</sup>

MacEtch is a wet etching process which offers controllability of structural parameters such as orientation, length, morphology, etc., and furthermore, a simple and low-cost way to fabricate extremely high aspect ratio semiconductor nanostructure.<sup>3</sup> This process uses the catalytic activity of noble metals (e.g. Au, Ag, or Pt) to etch silicon beneath it, in a mixed solution of an oxidant (e.g. hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)) and an acid (e.g. hydrogen fluoride (HF)).<sup>1,3</sup> Figure 1 depicts a schematic diagram of MacEtch process. Figure 2 shows the MacEtch process flow. As can be seen from figure 1, the electron holes are generated on the Au layer by the reduction of H<sub>2</sub>O<sub>2</sub> and are injected into the Si substrate at the interface between the Si and Au layer. HF will dissolve away the oxidized Si atom by forming silicon hexafluoride ion (SiF<sub>6</sub><sup>2-</sup>). The etch rate underneath the noble metal is much higher than that without the metal, due to the catalytic properties of noble metal, so that the metal layer descends into the semiconductor as the semiconductor is being etched right underneath.<sup>4</sup> This report describes fabrication of nanopillars ranging from 100 to 1000 nm using MacEtch process.

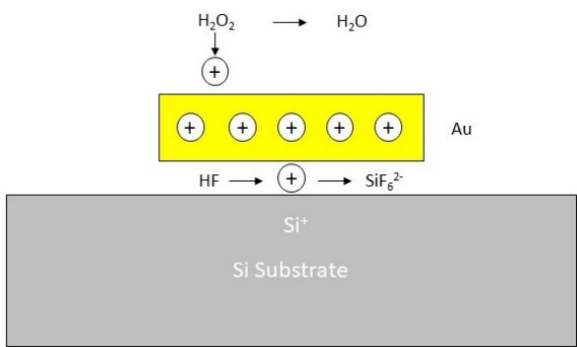


Figure 1. A schematic diagram of Metal Assisted Chemical Etching

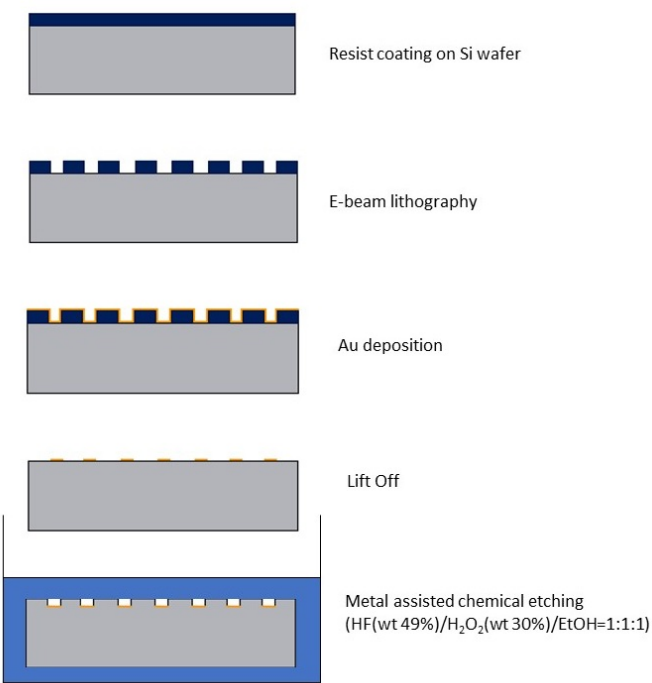


Figure 2: Process flow for metal assisted chemical etching

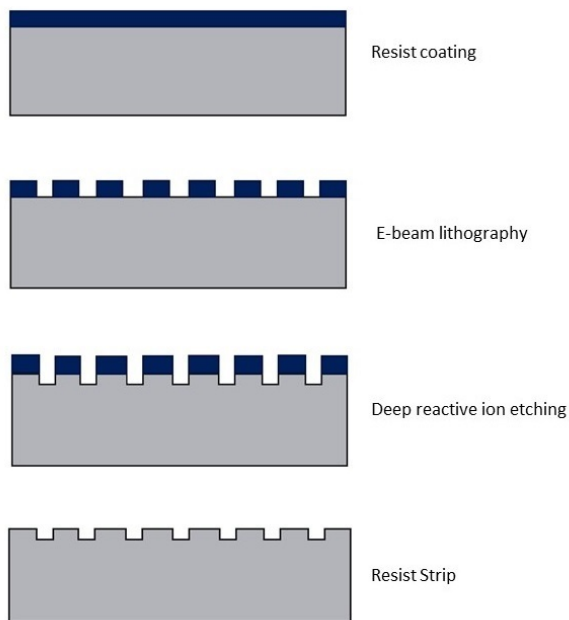


Figure 3. Process flow for deep reactive ion etching

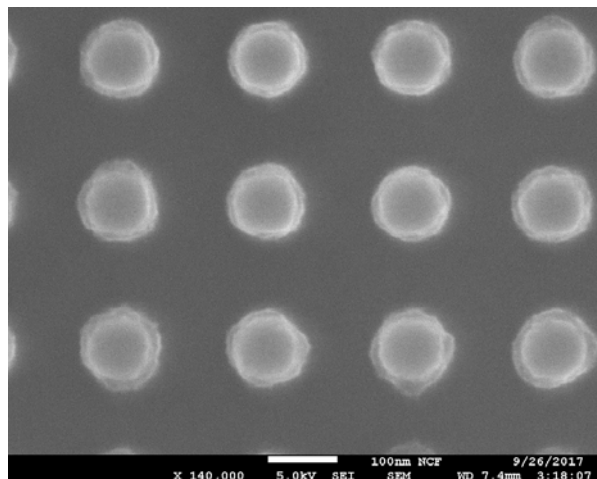


Figure 4: SEM showing developed HSQ sample

On the other hand, the Bosch process involves a sequence of alternating steps of (a) nearly isotropic silicon etching using  $\text{SF}_6$  plasma and (b) passivation of already etched silicon to prevent further etching using a chemically inert polymer (typically,  $\text{C}_4\text{F}_8$ ). The cycle is repeated to get an anisotropic vertical etching. As the cycle proceeds, it generates a ripple type structure with scalloping on the side wall.<sup>5,6</sup> For smaller feature size, the scallop size becomes comparable with the feature size and thus can pose a problem.<sup>7</sup> This report shows a way to get smooth side-walled silicon nanopillars using a little varied Bosch process by releasing both the etch gas ( $\text{SF}_6$ ) and passivation gas ( $\text{C}_4\text{F}_8$ ) at the same time.<sup>8</sup> The reaction takes place at lower temperature to control the etching and get anisotropic etch profile. Figure 3 shows the process flow for DRIE.

## 2. Experimental Section

### 2-1. Bosch Process

#### A. E-beam Lithography

The Si wafer was cleaned with Buffered Oxide Etch (BOE) bath for 1 min, followed by DI water rinse. Then, a 100 nm thick Hydrogen silsesquioxane (HSQ) film (a negative tone e-beam resist XR-1514, Dow Corning) was spin coated at 7000rpm for 1 sec, followed by 4000rpm for 45sec. The HSQ film was baked at 80 °C for 4 min on a hot plate. E-beam lithography was carried out using Elinox ELS-7500EX. The acceleration voltage was 50kV, the beam current was 100 pA, and the objective lens aperture was 40  $\mu\text{m}$ . The e-beam dose was 300  $\mu\text{C}/\text{cm}^2$ , and the dose time was 3  $\mu\text{sec}$  (for pitch size 2 using Beamer (GenISys))<sup>9</sup> in the area of 300 $\times$ 300  $\mu\text{m}^2$  with the total dots of 60000 $\times$ 60000. The HSQ film exposed was developed for 130 sec in CD-26 and the wafer was rinsed with gently flowing DI water for 90sec and was dried using nitrogen gun. Figure 4 shows a SEM image of the developed HSQ, indicating consistent features of 100nm.

#### B. Deep Reactive Ion Etching with and without Bosch Process and Resist Stripping

The Si substrate was dry-etched through developed HSQ film, using SPTS Rapier Si DRIE system in the following condition: process pressure = 40 mTorr;  $\text{SF}_6$  gas flow = 50 sccm;  $\text{C}_4\text{F}_8$  gas flow = 100 sccm; source power = 800 W; process time = 100 sec;  $T = -4^\circ\text{C}$ . Both  $\text{SF}_6$  and  $\text{C}_4\text{F}_8$  gases were flown simultaneously to create an anisotropic etch profile.<sup>8</sup> The etching depth was 212 nm, and the etching speed was 112 nm/min with the 80.4 % exposed area. Table 1 indicates the exposed area and the etch rate for the Bosch process in this study. On the other hand, the Si substrate was also dry-etched for comparison using Oxford 80 plus reactive ion etching (RIE) system in the following condition  $\text{SF}_6 = 50$  sccm;  $\text{O}_2 = 10$  sccm; process pressure = 150 mTorr; RF power = 100 W;  $T = 20^\circ\text{C}$ . On e-beam exposure the HSQ converts to  $\text{SiO}_2$ . So, RIE process using  $\text{CF}_4$  was used to strip the resist. It was done using Oxford 80 Plus RIE system in the

following condition: process pressure = 65 mTorr; RF power = 150 W; CF<sub>4</sub> flow rate = 20 sccm; process time = 160 sec; T = 15 °C.

Table 1. Exposed or Au coated areas and etch rates of the Bosch process and Metal Assisted Chemical Etching. The total area for the etching is 400 μm<sup>2</sup>.

Pillar diameter (nm)	Exposed or Au coated area (%)	Etch rate (nm/min)
<b>Bosch Process</b>		
100	80.4	112
<b>Metal Assisted Chemical Etching</b>		
100	95.1	34
200	87.4	40
400	73.6	58
600	62.6	65
800	40.7	71
1000	55.8	66

## 2-2. Metal Assisted Chemical Etching

### A. E-beam Lithography

The Si wafer was cleaned with BOE bath for 1 min, followed by DI water rinse. A 100 nm thick Poly(methyl methacrylate) (PMMA) film (a positive tone e-beam resist) was spin coated at 1500 rpm for 45 sec, followed by baking at 180 °C for 5 min on a hot plate. For e-beam lithography, the acceleration voltage was 50 kV, the beam current was 100 pA, and the objective lens aperture was 40 μm. The e-beam dose was 200 μC/cm<sup>2</sup>, and the dose time was 2 μsec (for pitch size = 2 using Beamer)<sup>6</sup> in the area of 300×300 μm<sup>2</sup> with the total dots of 60000×60000. The tone reversal was carried out on Beamer. The PMMA film exposed was developed for 60 sec in IPA:DI water (3:1) followed by rinsing in IPA for 60 sec.

### B. Au Deposition and Lift-off

5 nm and 20nm thick Au films were deposited onto the developed PMMA film under the base pressure of ~8.0 x 10<sup>-8</sup> Torr, using load lock PVD-75 e-beam evaporator (Kurt J. Lesker) at a deposition rate of 2.0 Å/sec. The PMMA film was removed using lift-off by sonicating the sample in acetone for few seconds, followed by drying using nitrogen gun, leaving behind only the Au film deposited directly on the Si wafer. Figure 5 shows SEM images of (a) the developed PMMA film, (b) the 5 nm thick Au film deposited on the developed PMMA film, and (c) the 20 nm thick Au film after the lift-off process.

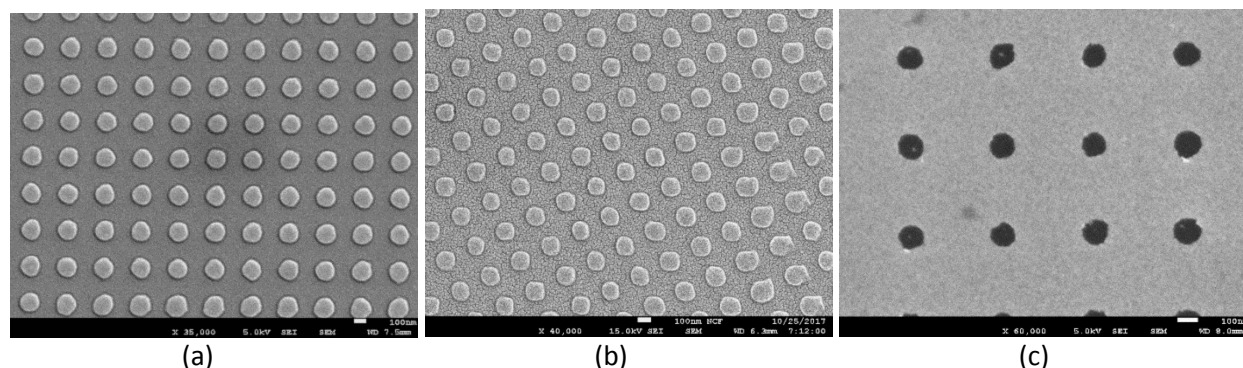



Figure 5. SEM images of (a) the developed PMMA film, (b) the 5 nm thick Au film deposited on the developed PMMA film, and (c) the 20 nm thick Au film after the lift-off process.



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### C. Metal Assisted Chemical Etching:

For performing the MacEtch, the Si wafer with Au pattern was immersed in 1:1:1 (v/v) mixture of ethanol, HF (49 wt%) and H<sub>2</sub>O<sub>2</sub> (30 wt%) for 5 min. The sample was then rinsed with DI water, and dried using a nitrogen gun. Table 1 also shows the Au coated areas, which are etched by MacEtch, and the etch rates.

## 3. Results and discussion

### 3-1. Bosch Process

Figure 6 shows SEM images of the (a) corner and (b) center of the patterned area etched by the Bosch process in this study. The etching and passivation gases were simultaneously released to avoid the ripple structure<sup>6</sup> by the typical Bosch process, resulting in smooth vertical side walls of the pillars, as seen in figure 6. On the other hand, the verticality of the pillars at the corner of the patterned area in figure 6(a) is much better than that at the center of the patterned area in figure 6(b). It is assumed that this may be caused by the lower availability of etch gases at the center of the wafer owing to the presence of features surrounding it from all the sides when compared with the corner of the wafer. Figure 7 shows SEM images of the silicon wafer etched by a deep Si etch recipe of the regular RIE process with SF<sub>6</sub> gas, indicating that the etching is isotropic and no vertical silicon nanopillars are obtained.

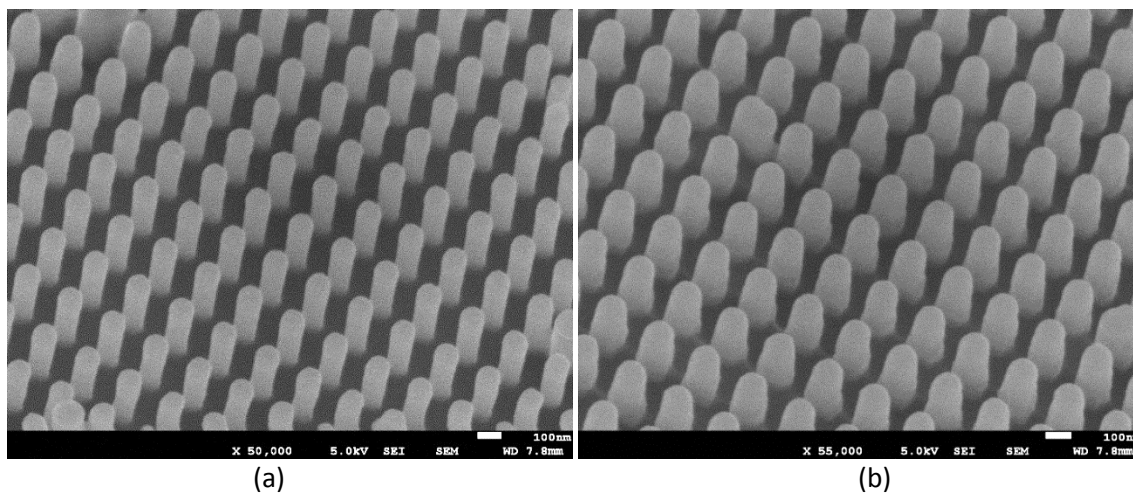


Figure 6. SEM images of (a) the corner and (b) the center of the patterned area etched by Bosch process

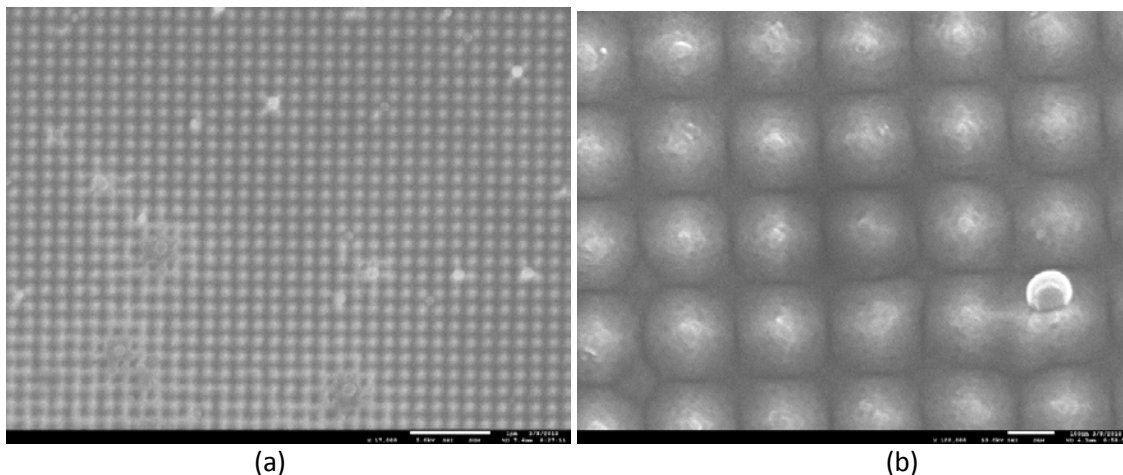


Figure 7. SEM images of Si wafer using regular RIE process: (a) x17,000; (b) x200,000.

### 3-2. Metal assisted chemical etching

Figure 8 shows SEM image of 5 nm thick Au coated area etched by MacEtch. As can be seen from figure 8, the Si surface is heavily etched and became porous, with porous sizes bigger than the feature size and thus no silicon nanopillars was

obtained using this recipe. The reagent and byproduct diffuse along the interface between the noble metal and the Si substrate during the etching process, which reproduces the previous result.<sup>4</sup> It is speculated that the Au film was too thin and must have been broken by the mass transfer through the Au film and has collapsed the Au film, resulting in heavy etching of the Si wafer.<sup>3,4</sup>

Figure 9 shows SEM images of the 20 nm thick Au coated area etched by MacEtch, revealing silicon nanopillars with the diameters of (a) 100, (b) 200, (c) 400, (d) 600, (e) 800, and (f) 1000 nm, as the patterns designed. With the 20nm thick Au layer, the side wall is etched vertically, and no porous structure is seen, although the top part of the silicon pillars has some porosity, manifesting that the 20nm thick Au film can handle mass transfer more efficiently and does not collapse during the process. It is assumed that the porosity on the top part is

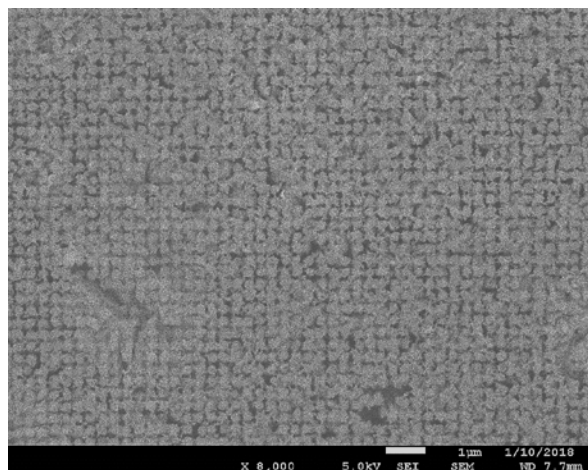


Figure 8: SEM image showing MacEtch process with 5nm Au layer for 100nm feature size.

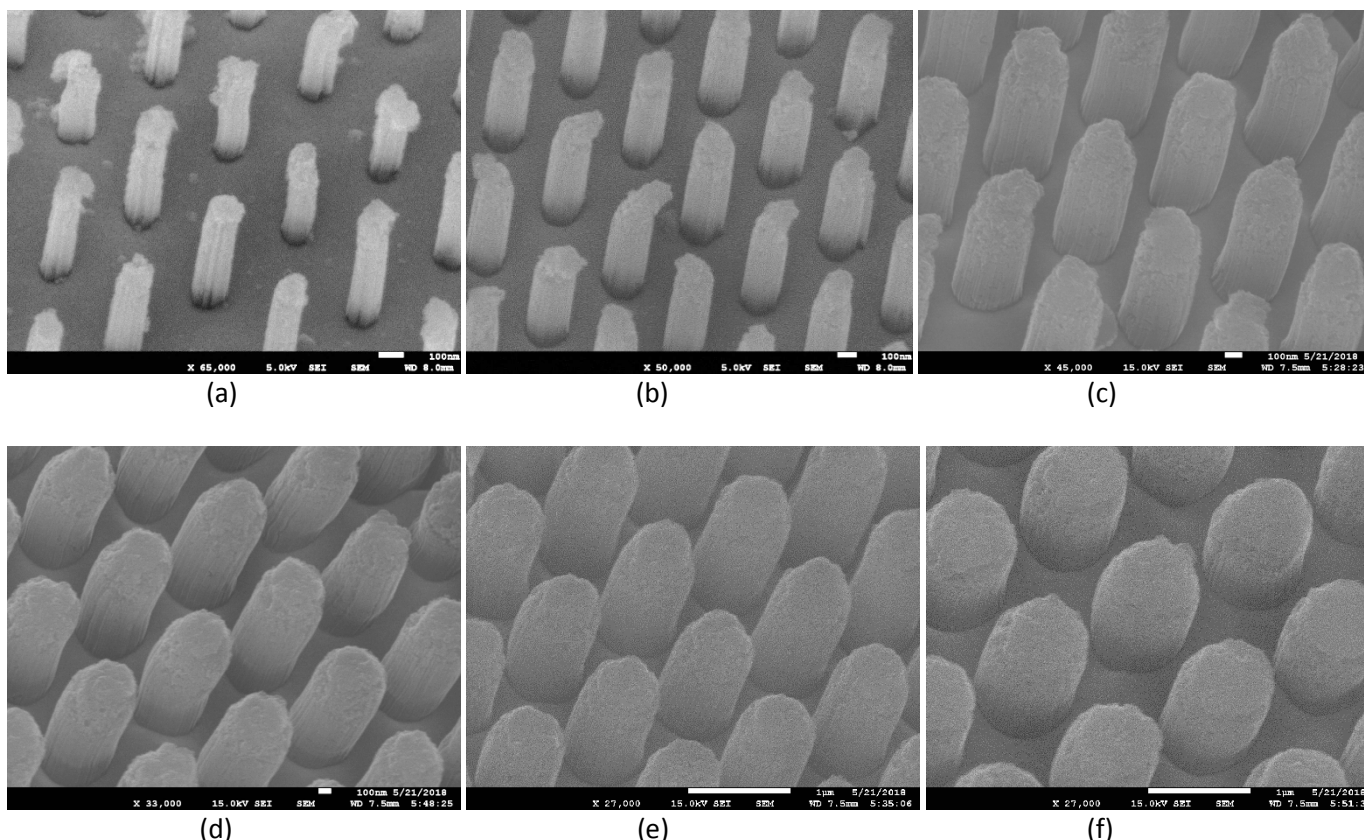



Figure 9: SEM image of Si nanopillar after MacEtch process for (a) 100nm; (b) 200nm; (c) 400nm; (d) 600nm; (e) 800nm and (f) 1000nm.

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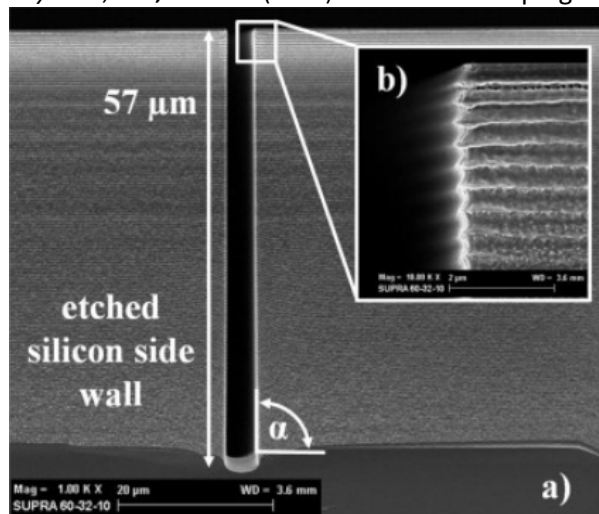
attributed to a longer exposure time into the solution when compared to the bottom part, which result in more damage by the mass transfer through the Au film. On the other hand, the etch rate increases with increasing in the feature size, as indicating in Table 1, due to the larger pass way of the mass transfer.

#### 4. Summary

Nanopillars fabricated by MacEtch wet-etch process have been compared with those by Bosch dry-etch process. The Bosch process in this study gave vertical nanopillars with smooth side walls, which was better than the typical Bosch process. However, the verticality of the nanopillars depended on the location where to be etched. On the other hand, MacEtch process can etch Si material much simpler and cheaper without an expensive etching tool. This study showed that MacEtch process gave a very consistent feature using 20 nm thick Au film, but the top of the pillar was still porous and not smooth. Further investigation is needed on some parameters, *e.g.* Au film thickness and etching solution, for the better feature.

#### References

- <sup>1</sup> R. Kapadia *et al.*, "Nanopillar photovoltaics: Materials, processes, and devices", *Nano Energy*, **1**, 132-144(2012).
- <sup>2</sup> B.Q. Wu *et al.*, "High aspect ratio silicon etch: A review", *J. Appl. Phys.* 108, 051101(2010).
- <sup>3</sup> Z. Huang *et al.*, "Metal-assisted chemical etching of silicon: A review", *Advanced Materials*, **23**, 285–308 (2011).
- <sup>4</sup> I. Bajwa, Technical Report (Graduate Student Fellow Program) Metal Assisted Chemical Etching (2016).  
[https://repository.upenn.edu/scn\\_protocols/26/](https://repository.upenn.edu/scn_protocols/26/)
- <sup>5</sup> F. Laermer, & A. Schilp, "Method of anisotropically etching silicon", *US Patent 6284148* 7 (1996). doi:US5501893 A
- <sup>6</sup> M. Nowack *et al.*, "Micro arc welding for electrode gap reduction of high aspect ratio microstructures", *Sensors and Actuators, A: Physical.*, **188**, 495–502(2012). See the scalloping side wall after typical Bosch process below.



- <sup>7</sup> S. Tachi *et al.*, "Low-temperature reactive ion etching and microwave plasma etching of silicon", *Appl. Phys. Lett.*, **52**, 616–618 (1988).
- <sup>8</sup> G. S. Kim, Personal communication.
- <sup>9</sup> If the pitch size is 1, then the dose time is 0.75 μsec.